Voltaic Cells and Reduction Potential Problems

A voltaic cell is constructed that has one electrode compartment consisting of an aluminum strip and a 1.0 *M* solution of $Al(NO_3)_3$. The other compartment has a nickel strip placed in a solution of $NiSO_4$. Using the table of standard reduction potentials (SRP), **(a)** write the overall reaction taking place in the cell. **(b)** What is being oxidized, and what is being reduced? **(c)** Write the half-reactions occurring in each compartment. **(d)** Which electrode is the cathode, which is the anode? **(e)** Indicate the charges of each electrode. **(f)** In which direction do the electrons flow? **(g)** In which directions do the ions flow through the salt bridge? **(h)** Write the line notation for this cell.

a $2Al + 3Ni^{2+} \rightarrow 2Al^{3+} + 3Ni$

b Al ox Ni^{2+} Red

c anode $Al \rightarrow Al^{3+} + 3e^-$

Cath $Ni^{2+} + 2e^- \rightarrow Ni$

d anode → Al
cath → Ni

e anode + cath (−)

f from anode to cathode

g + ions flow into Ni^{2+} soln
(−) ions flow into Al^{3+} soln

h $Al|Al^{3+}||Ni^{2+}|Ni$

Using SRPs calculate the standard emf for each of the following reactions.

(a) $Cl_2(g) + I^-(aq) \rightarrow Cl^-(aq) + I_2(s)$
(b) $Ba^{2+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Ba(s)$
(c) $Fe(s) + Fe^{3+}(aq) \rightarrow Fe^{2+}(aq)$

(a) $Cl_2 + 2e^- \rightarrow 2Cl^-$ $\mathcal{E}^\circ = +1.36V$
$2I^- \rightarrow I_2 + 2e$ $\mathcal{E}^\circ = -0.54V$
$\mathcal{E}^\circ_{cell} = +0.82$

(b) $Ba^{2+} + 2e^- \rightarrow Ba$ $\mathcal{E}^\circ = -2.90V$
$Cu \rightarrow Cu^{2+} + 2e$ $\mathcal{E}^\circ = -0.34V$
$\mathcal{E}^\circ_{cell} = 3.24$

(c) $Fe \rightarrow Fe^{2+} + 2e^-$ $\mathcal{E}^\circ = +0.44V$
$2e^- + 2Fe^{3+} \rightarrow 2Fe^{2+}$ $\mathcal{E}^\circ = +0.77V$
$\mathcal{E}^\circ_{cell} = +1.21V$

Use SRPs to determine which is the stronger oxidizing agent.

$Cl_2(g)$ or $Br_2(l)$ $Ni^{2+}(aq)$ or $Cd^{2+}(aq)$ $IO_3^-(aq)$ or $Cr_2O_7^{2-}(aq)$ $O_2(g)$ or $Cl_2(g)$

Use SRPs to determine which is the stronger reducing agent.

Fe(s) or Mg(s) Ca(s) or Al(s) $F_2(aq)$ or $I_2(aq)$ Ag(s) or Cu(s) $MnO_4^-(aq)$ or Fe(s)

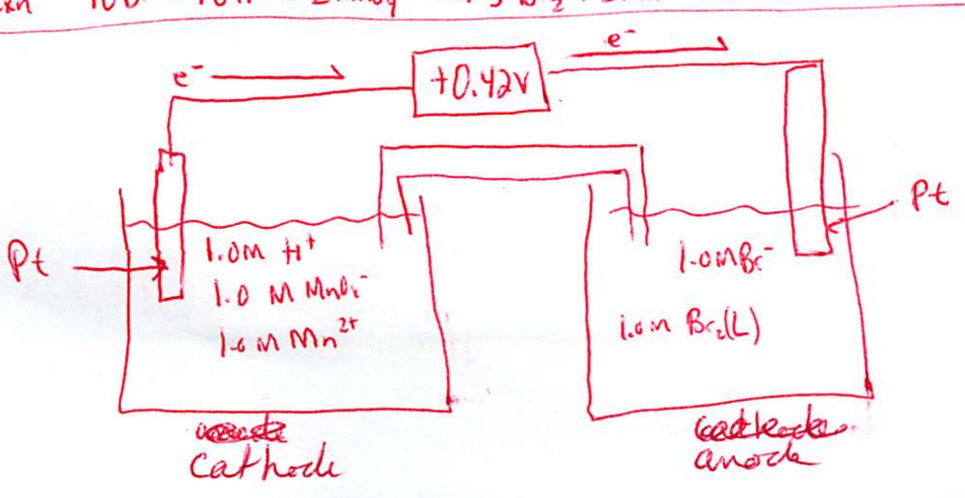
Sketch and describe the voltaic cell that takes place for the following reaction:

$Br^-(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + Br_2(l)$

(anode) $10Br^- \rightarrow 5Br_2 + 10e^-$ $\mathcal{E}^\circ = -1.09V$

(cathode) $10e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O$ $\mathcal{E}^\circ = +1.51V$

$\boxed{\text{Cell Rxn } 10Br^- + 16H^+ + 2MnO_4^- \rightarrow 5Br_2 + 2Mn^{2+} + 8H_2O \ \mathcal{E}^\circ = +0.42V}$



Free Energy, Equilbrium, and Redox Problems

For each of the following reactions, write a balanced equation, calculate E^o for each cell, calculate ΔG^o at 298 K, and calculate the equilibrium constant for each reaction at 298 K.

(a) Aqueous iodide ion is oxidized by silver metal ion
(b) In acidic solution, copper (I) ion is oxidized by nitrate ion.
(c) In basic solution, solid cromium (III) hydroxide is oxidized by hypochlorite ion.

a $2I^- \rightarrow I_2 + 2e^-$ $\mathcal{E}^\circ = -0.54V$

$2e^- + 2Ag^+ \rightarrow 2Ag$ $\mathcal{E}^\circ = +0.80V$

$\boxed{\mathcal{E}^\circ_{cell} = +0.26V}$

$\Delta G = -(2)\, 96500\frac{J}{mole}\,(0.26\frac{J}{C})$

$= -5.0\times10^4\ J = \boxed{-50.\ kJ}$

$K = e^{\frac{-50000J}{(R)(298)}} = \boxed{6.2\times10^8}$

b $3Cu^+ \rightarrow 3Cu^{2+} + 3e^-$ $\mathcal{E}^\circ = -0.16V$

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ $\mathcal{E}^\circ = 0.96V$

$\boxed{+0.80V}$

$\Delta G = -(3)(96500\frac{C}{mol})(0.80V)$

$= -2.3\times10^5\ J = \boxed{-230kJ}$

$K = e^{\frac{-2.3\times10^5 J}{-R(298)}} = \boxed{1.9\times10^{40}}$

c $Cr(OH)_3 + H_2O \rightarrow Cr_2O_7^{2-} + 4H^+$ → Bal

$4H^+ + 2e^- + 2ClO^- \rightarrow Cl_2 + 2H_2O$

$\mathcal{E}^\circ_{cell} = 0 - 0.44V$

$\Delta G = -(6)(96500\frac{C}{mol})(-0.44V)$

$= 2.5\times10^5\ J = \boxed{250\ J}$

$K = e^{\frac{2.5\times10^5 J}{-R\,298}} = \boxed{2.2\times10^{-45}}$

At 298 K a cell reaction has a standard electrode potential of +0.17 V. The equilibrium constant for the cell reaction is 5.5×10^5. What is the value of n for the cell reaction?

$\Delta G^\circ = -RT\ln K$

$(-8.315\frac{J}{mol\,K})(298K)(\ln 5.5\times10^5)$

$-3.3\times10^4\ kJ$

$\Delta G = -n\mathcal{F}\mathcal{E}^\circ$

$n = \frac{-3.3\times10^4\ kJ}{(-96500)(+0.17V)}$

$= \boxed{2}$

Predict whether the following reactions will be spontaneous under standard conditions:

(a) oxidation of Sn to Sn^{2+} by I_2
(b) reduction of Ni^{2+} to Ni by I^-
(c) reduction of Cu^{2+} to Cu by Fe^{2+}

a $Sn \rightarrow Sn^{2+} + 2e^-$ $\mathcal{E}^\circ = 0.14V$

$2e^- + I_2 \rightarrow 2I^-$ $\mathcal{E}^\circ = 0.54V$

$\mathcal{E}^\circ = 0.68V$

spontaneous

b $Ni^{2+} + 2e^- \rightarrow Ni$ $\mathcal{E}^\circ = -0.23V$

$2I^- \rightarrow I_2 + 2e^-$ $\mathcal{E}^\circ = -0.54V$

$\mathcal{E}^\circ = -0.77V$

nonspontaneous

c $Cu^{2+} + 2e^- \rightarrow Cu$ $\mathcal{E}^\circ = 0.34V$

$2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$ $\mathcal{E}^\circ = -0.77$

$\mathcal{E}_{cell} = -0.43$

Calculate the equilibrium constant for the disproportionation of the copper (I) ion to copper metal and copper (II) ions.

$Cu^+ \rightarrow Cu^{2+} + Cu$

$Cu^+ + e^- \rightarrow Cu$ $\mathcal{E}^\circ = 0.52V$

$Cu^+ \rightarrow Cu^{2+} + e^-$ $\mathcal{E}^\circ = -0.16V$

$\mathcal{E}_{cell} = 0.36V$

$\Delta G = -nFE = -RT\ln K$

$\frac{(1)(96500C)(0.36V)}{(8.315\frac{J}{mol\,K})(298K)} = \ln K$

$\boxed{1.2\times10^6 = K}$

$\cancel{H_2O} + 2Cr(OH)_3 \rightarrow Cr_2O_7^{2-} + 8H^+ + \cancel{6e^-}$ $\quad \mathcal{E} = 1.33V$

$6 \quad\quad \cancel{12}$

$\cancel{2e^-} + \cancel{4H^+} + \cancel{2}ClO^- \rightarrow 3Cl_2 + \cancel{2}H_2O$ $\quad \cancel{6}\,5$

1
$4H_2O$

$\cancel{4H^+} + 2Cr(OH)_3 + 6ClO^- \rightarrow Cr_2O_7^{2-} + 3Cl_2 + \cancel{5H_2O}\ OH^-$

$\cancel{H_2O} + 2Cr(OH)_3 \rightarrow Cr_2O_7^{2-} + \cancel{8H^+} + \cancel{6e^-}$ $\quad \mathcal{E}^\circ = -1.33V$

$4 \quad \cancel{12} \quad 6 \quad\quad \cancel{6}\,5$

$\cancel{2e^-} + \cancel{4H^+} + \cancel{2}ClO^- \rightarrow 3Cl_2 + \cancel{2}H_2O$ $\quad \mathcal{E}^\circ = +0.89V$

$+4OH^- \quad\quad\quad +4OH^-$

$\cancel{4H_2O} + 2Cr(OH)_3 + 6ClO^- \rightarrow Cr_2O_7^{2-} + 3Cl_2 + 4OH^- + 8H_2O$ $\quad \mathcal{E}_{cell} = -0.44V$

Nernst Equation Problems

$\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \log Q$

A galvanic cell utilizes the following reaction:

$$Al(s) + 3Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3Ag(s)$$ $Q = \frac{[Ag]^3}{[Al^{3+}]}$

What is the effect on the cell potential if each of the following changes? (a) Water is added to the anode compartment. (b) The size of the aluminum electrode increases. (c) A solution of $AgNO_3$ is added to the cathode compartment, increasing the quantity of the Ag^+ but not changing its concentration. (d) HCl is added to the compartment containing $AgNO_3$.

(a) $\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \left(\log \frac{[Al^{3+}]\downarrow}{[Ag^{3+}]}\right)$

$[Al^{3+}]\downarrow$ when diluted thus $Q\uparrow$ (−)

and $\mathcal{E}\uparrow$

(b) No change b/c the Al(s) does not factor into Q

(c) No $[Ag^+]$ change No change in cell volatage

(d) $\mathcal{E} = \mathcal{E}^\circ - \frac{0.0591}{n} \left(\log [Ag^+]^3 \downarrow\right)$

$[Ag]\downarrow$ so $Q\downarrow$ makes $\log Q$ (−) and $\mathcal{E}\uparrow$

A galvanic cell utilizes the following reaction:

$$Pb(s) + Sn^{2+}(aq) \rightarrow Pb^{2+}(aq) + Sn(s)$$

$\mathcal{E}^\circ = -0.14V$

$\mathcal{E}^\circ = 0.13V$

$\mathcal{E}^\circ_{cell}$ 0.01V

If the concentration of Sn^{2+} in the cathode compartment is 1.00 *M* and the cell generates a potential of +0.22 V, what is the concentration of Pb^{2+} in the anode compartment? If the anode compartment contains $[SO_4^{2-}] = 1.00$ *M* in equilibrium with $PbSO_4(s)$, what is the K_{sp} of $PbSO_4$? 20.66 in white

$0.22V = -0.01V - \frac{0.0591}{2}\left(\log \frac{x}{1.00M}\right)$

$\log x = -7.8$

$x = \boxed{1.6\times10^{-8} M = [Pb^{2+}]}$

$K_{sp} = (1.6\times10^{-8} M)(1.0 M)$

$= \boxed{1.6\times10^{-8} M}$

Electrolysis Problems

A Cr^{3+}(aq) solution is electrolyzed using a current of 7.60 A. What mass of Cr(s) is plated out after 2.00 days? What amperage is required to plate out 0.250 mol Cr from a Cr^{3+} solution in a period of 8.00 h?

$Cr^{3+} + 3e^- \rightarrow Cr$

$2.00\,days \times \frac{24\,hrs}{1\,day} \times \frac{3600\,s}{1\,hr} \times \frac{7.6\,C}{s} \times \frac{1\,mol\,e^-}{96500\,C} \times \frac{1\,mol\,Cr}{3\,mol\,e^-} \times \frac{52.0\,g\,Cr}{mol\,Cr} = \boxed{235\,g\,Cr}$

$8.00\,hr \times \frac{3600\,s}{1\,hr} = 2.88\times10^5\,s$

$0.250\,mol \times \frac{3e^-}{1\,mol\,Cr} \times \frac{96500\,C}{1\,mol\,e} = \frac{7.24\times10^4\,C}{2.88\times10^5\,s}$

$= \boxed{0.251\,A}$

Metallic magnesium can be made by the electrolysis of molten magnesium chloride. What mass of Mg is formed by passing a current of 5.25 A through molten $MgCl_2$ for 2.50 days? How many minutes are needed to plate out 10.00 g Mg from molten $MgCl_2$, using 3.50 A of current?

$Mg^{2+} + 2e^- \rightarrow Mg$

$2.50\,d \times \frac{24\,hr}{1\,day} \times \frac{3600\,s}{1\,hr} \times \frac{5.25\,C}{s} \times \frac{1\,mol\,e^-}{96500\,C} \times \frac{1\,mol\,Mg}{2\,mol\,e^-} \times \frac{24.3\,g\,Mg}{1\,mol\,Mg} = \boxed{142\,g}$

$10.0\,g\,Mg \times \frac{1\,mol\,Mg}{24.3\,g\,Mg} \times \frac{2\,mol\,e}{1\,mol\,Mg} \times \frac{96500\,C}{1\,mol\,e} \times \frac{1\,s}{3.50\,C} \times \frac{1\,min}{60\,s} = \boxed{378\,min}$